

## Electronic Supplementary Material

# Energy-efficient recovery of tetrahydrofuran and ethyl acetate by triple-column extractive distillation: entrainer design and process optimization

Ao Yang<sup>1,2</sup>, Yang Su<sup>3</sup>, Tao Shi<sup>2</sup>, Jingzheng Ren<sup>2</sup>, Weifeng Shen (✉)<sup>1</sup>, Teng Zhou (✉)<sup>4,5</sup>

1 School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 401331, China

2 Department of Industrial and Systems Engineering, The Hong Kong Polytechnic University, Hong Kong, China

3 School of Intelligent Technology and Engineering, Chongqing University of Science & Technology, Chongqing 401331, China

4 Process Systems Engineering, Otto-von-Guericke University Magdeburg, D-39106 Magdeburg, Germany

5 Process Systems Engineering, Max Planck Institute for Dynamics of Complex Technical Systems, D-39106 Magdeburg, Germany

E-mails: shenweifeng@cqu.edu.cn (Shen W); zhout@mpi-magdeburg.mpg.de (Zhou T)

**Table S1.** The values of  $R_j$  and  $Q_j$  of groups considered in CAMD

Group ID	Group $j$	$R_j$	$Q_j$
1	CH <sub>3</sub>	0.6325	1.0608
2	CH <sub>2</sub>	0.6325	0.7081
3	CH	0.6325	0.3554
4	C	1.6325	0.0000
14	OH(P)	1.2302	0.8927
15	CH <sub>3</sub> OH	0.8585	0.9938
16	H <sub>2</sub> O	1.7334	2.4561
18	CH <sub>3</sub> CO	1.7048	1.6700
19	CH <sub>2</sub> CO	1.7048	1.5542
20	CHO	0.7173	0.7710
21	CH <sub>3</sub> COO	1.2700	1.6286
22	CH <sub>2</sub> COO	1.2700	1.4228
23	HCOO	1.9000	1.8000
24	CH <sub>3</sub> -O	1.1434	1.6022
25	CH <sub>2</sub> -O	1.1434	1.2495
26	CH-O	1.1434	0.8968
27	THF	1.7023	1.8784
61	Furfural	1.2990	1.2890

67	DMSO	3.6000	2.6920
72	DMF	2.0000	2.0930
81	OH(S)	1.0630	0.8663
82	OH(T)	0.6895	0.8345

**Table S2.** Upper and lower bounds of the discrete and continuous decision variables

Variable	Direct TCED		Indirect TCED	
	Lower bound	Upper bound	Lower bound	Upper bound
$N_{T1}$	40	45	15	25
$N_{FE1}$	2	10	2	10
$N_{F1}$	10	20	5	15
$N_{T2}$	14	18	25	35
$N_{FE2}$	2	8	/	/
$N_{F2}$	5	12	10	20
$N_{T3}$	14	20	12	20
$N_{F3}$	3	10	3	10
$F_E$ (kmol/h)	50	200	10	150
SR	0.1	0.5	/	/
$D_1$ (kmol/h)	32.9	33.1	65.9	66.1
$RR_1$	0.01	15	0.01	10
$D_2$ (kmol/h)	32.9	33.1	32.9	33.1
$RR_2$	0.01	20	0.01	20
$D_3$ (kmol/h)	33.9	34.1	33.9	34.1
$RR_3$	0.01	10	0.01	10

**Table S3.** Results of the CAMD of entrainers for mixtures of EtAC-water and THF-water

$w_1$	EtAC-water				THF-water			
	$S_{AB}^\infty$	$C_B^\infty$	Objective function	Entrainer	$S_{AB}^\infty$	$C_B^\infty$	Objective function	Entrainer
1.0	17.13	0.0004	17.127	Furfural	7243.7	0.179	7243.7	Furfural
0.9	17.13	0.0004	15.415	Furfural	7243.7	0.179	6519.3	Furfural
0.8	17.13	0.0004	13.702	Furfural	7243.7	0.179	5795.0	Furfural
0.7	17.13	0.0004	11.989	Furfural	7243.7	0.179	5070.6	Furfural
0.6	17.13	0.0004	10.277	Furfural	7243.7	0.179	4346.3	Furfural
0.5	17.13	0.0004	8.564	Furfural	7243.7	0.179	3621.9	Furfural
0.4	17.13	0.0004	6.851	Furfural	7243.7	0.179	2897.6	Furfural
0.3	17.13	0.0004	5.138	Furfural	7243.7	0.179	2173.2	Furfural

0.2	17.13	0.0004	3.426	Furfural	7243.7	0.179	1448.9	Furfural
0.1	17.13	0.0004	1.713	Furfural	7243.7	0.179	724.5	Furfural
0.0	0.016	0.0034	0.003	DMF	0.0451	0.226	0.226	DMSO

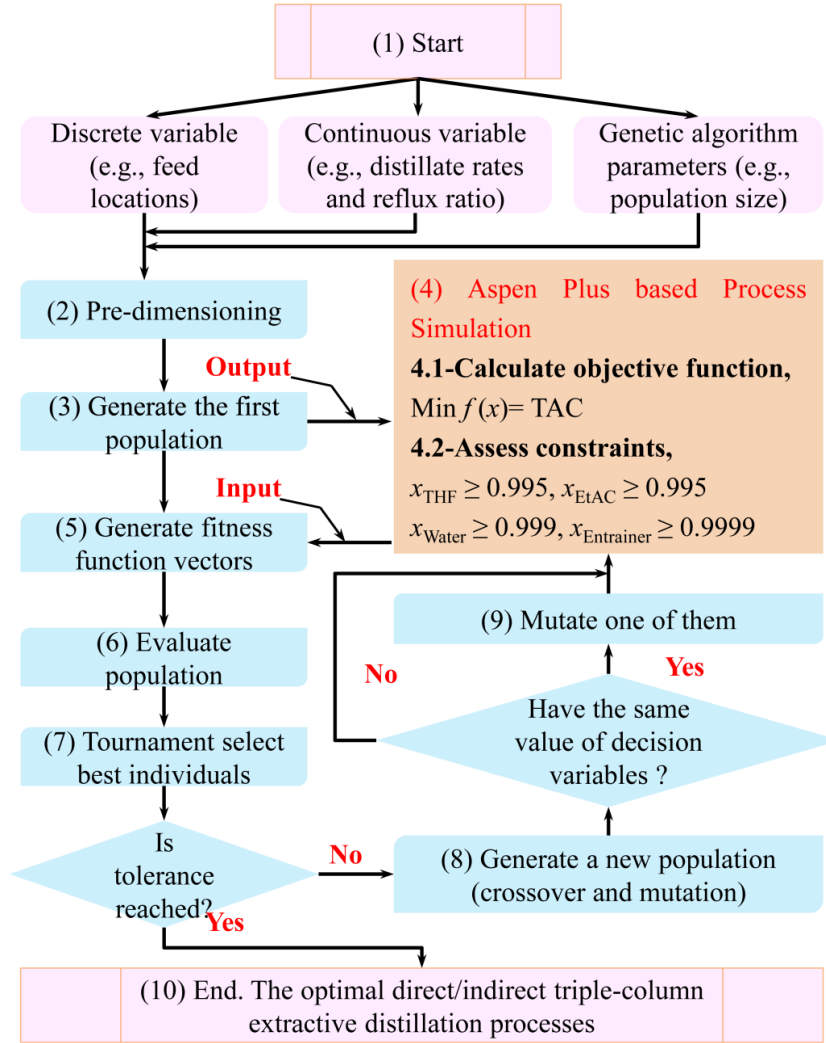
**Table S4.** The UNIQUAC binary interaction parameters of the studied

THF/EtAC/Water/DMSO system

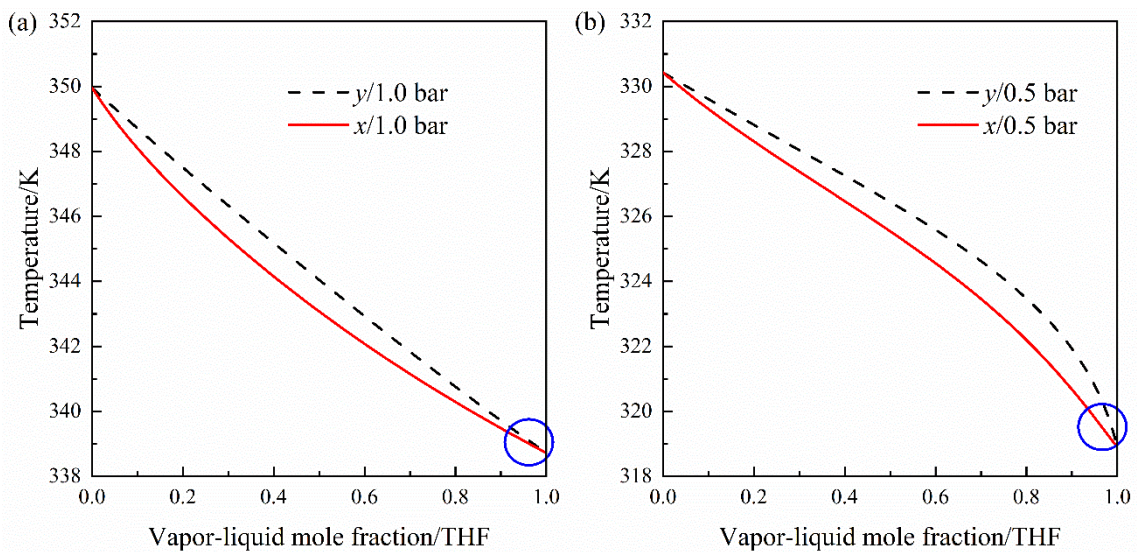
Comp. i	THF	THF	EtAC	THF	EtAC	Water
Comp. j	EtAC	Water	Water	DMSO	DMSO	DMSO
Source	[1]	APV84 VLE-IG	APV84 LLE-LIT	APV84 VLE-IG	APV84 VLE-IG	APV84 VLE-IG
A <sub>ij</sub>	7.456	0.3120	2.721	0.000	0.000	0.300
A <sub>ji</sub>	-14.348	-0.3878	-2.053	0.000	0.000	-0.730
B <sub>ij/K</sub>	-2354.860	-611.058	-1212.890	-159.818	-200.062	36.264
B <sub>ji/K</sub>	4638.790	236.118	531.033	-5.790	35.086	483.490

**Table S5.** The setup parameters of the improved GA used in the optimization process [2]

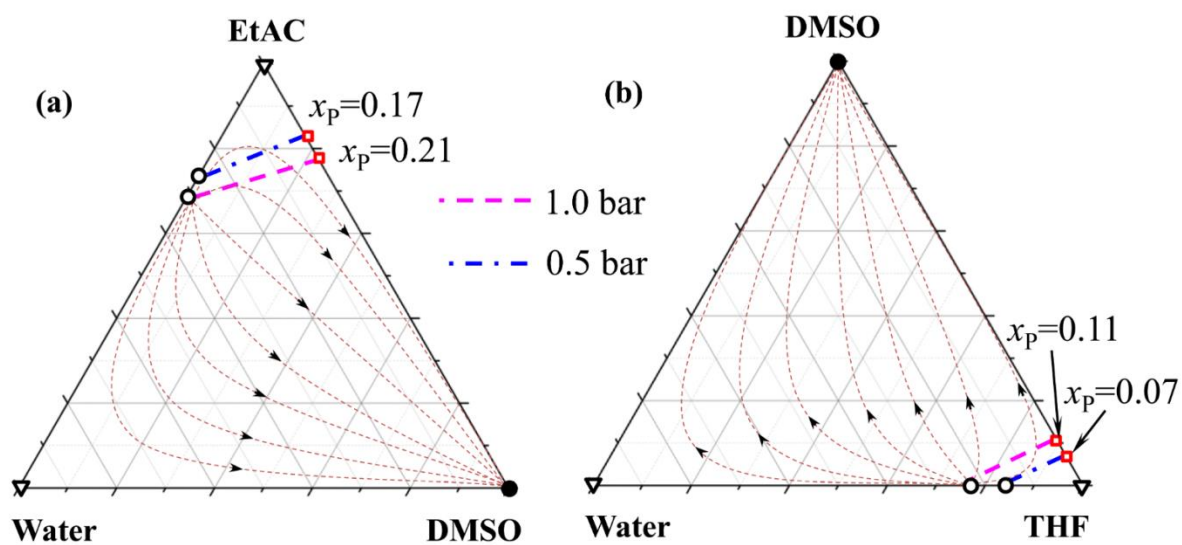
	Method	Parameter
Population size	/	<i>popSize</i> = 100
Restriction handle method	Dominance based method	<i>Niching</i> = yes
Selection method	Binary tournament	Tournament size = 2
Crossover operator	SBX	/
Crossover probability	/	0.95
Mutation operator	Polynomial	/
Mutation probability	/	0.1
Stopping criteria	Tolerance	$< 10^{-5}$



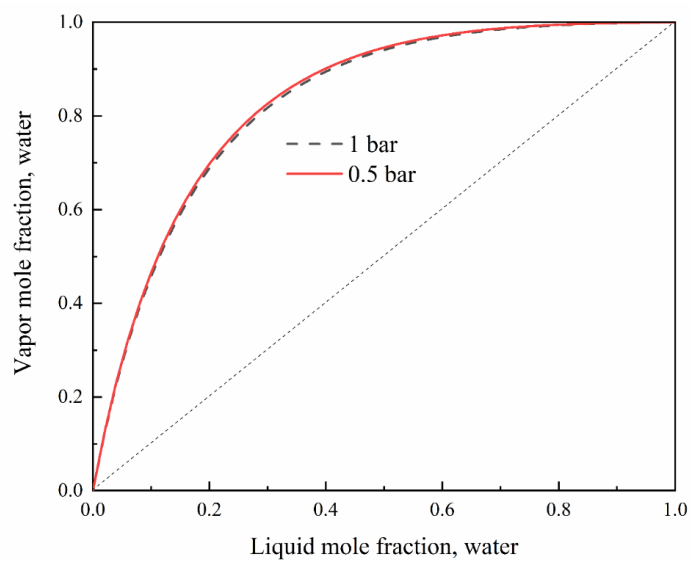
**Fig. S1** Process optimization using the improved GA approach



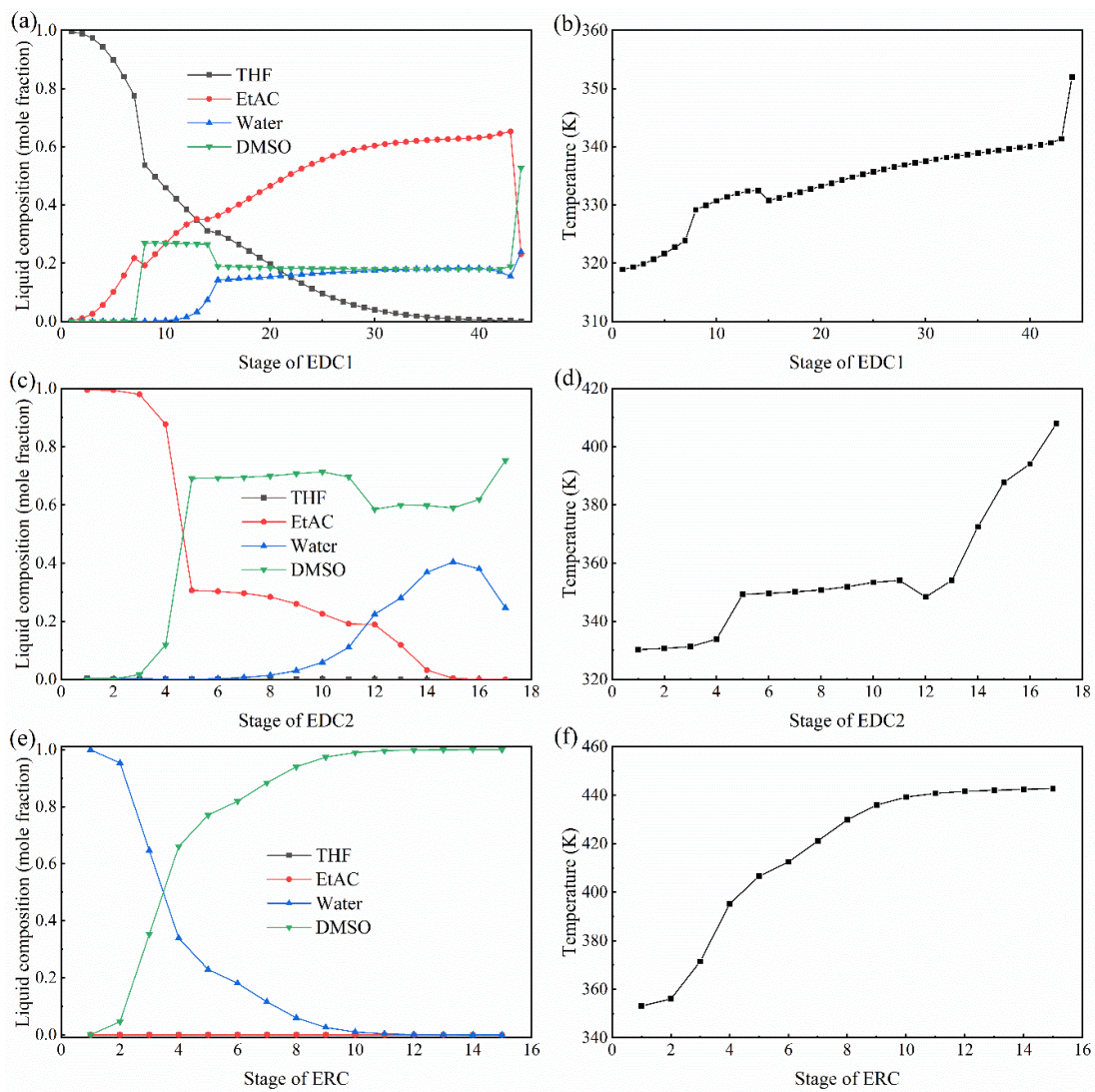
**Fig. S2** T-xy diagram for THF-EtAC under (a) 1.0 bar and (b) 0.5 bar



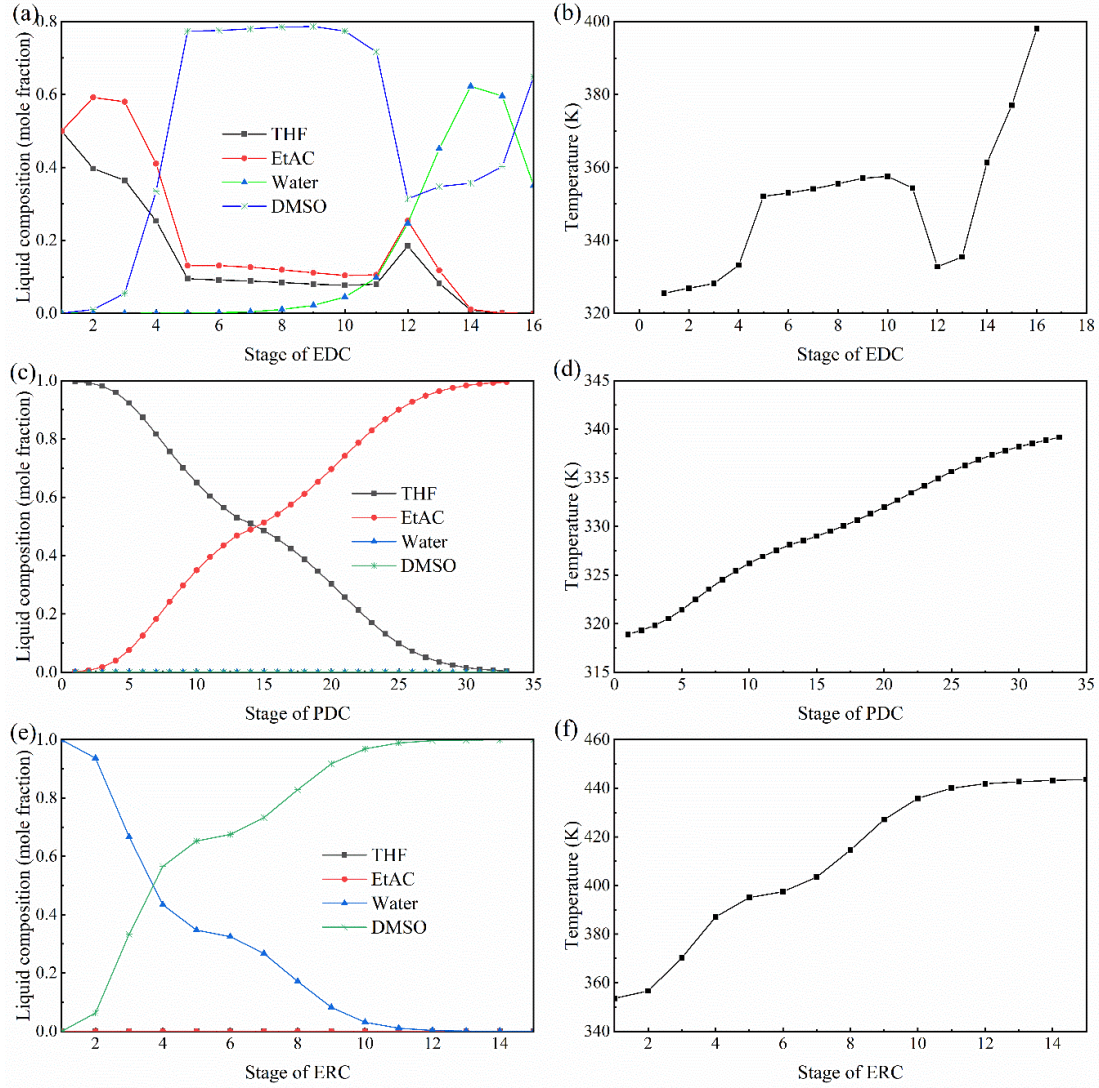
**Fig. S3** Univolatility lines of the (a) EtAC-water-DMSO and (b) THF-water-DMSO systems under 1.0 bar and 0.5 bar



**Fig. S4**  $x$ - $y$  diagram for the water/DMSO binary system



**Fig. S5** Liquid composition and temperature profiles of the direct TCED process



**Fig. S6** Liquid composition and temperature profiles of the indirect TCED process

### Cost determination

The column internal diameters (ID in m) could be obtained *via* the tray sizing tool in Aspen Plus. The calculation of column height (H in m) is shown as follows,

$$H = (N_T - 3) \times 0.609 \quad (S1)$$

where  $N_T$  denotes the total number of stages including condenser and reboiler.

Following the study of Luyben [3], shell and tray costs of all columns (assumed as sieve-tray column) are calculated *via* Eqs. S2-S3. Herein, the Marshall and Swift index (M&S)

of 1518.1 is employed [4].

$$\text{Shell cost} = \left( \frac{M \& S}{280} \right) \times 101.9 ID^{1.066} H^{0.802} \times (2.18 + F_C) = 2252.28 ID^{1.066} H^{0.802} \quad (S2)$$

$$\text{Tray cost} = \left( \frac{M \& S}{280} \right) \times 4.7 ID^{1.55} H \times F_C = 1423.7 ID^{1.55} H \quad (S3)$$

where correction factors of the shell and tray ( $F_C$ ) are determined as 1.9 and 55.9, respectively [3].

The cost of heat exchangers (HEC) including reboiler, condenser and cooler is calculated via the heat transfer area ( $A$  in  $m^2$ ) in Eq. S4.

$$HEC = \left( \frac{M \& S}{280} \right) \times 101.3 A^{0.65} \times (2.29 + F_C) = 9367.8 A^{0.65} \quad (S4)$$

TCC as shown in Eq. S5 is the summation of the shell cost, tray cost, and HEC while the calculation of AOC can be refer to Eq. S6.

$$TCC = \text{Shell cost} + \text{Tray cost} + HEC \quad (S5)$$

$$AOC = (C_{CW} \times Q_C + C_{\text{Steam}} \times Q_R) \times 8000 \times 3.6 \quad (S6)$$

where the price of cooling water is represented as  $C_{CW}$ , which is assumed as 0.354 US\$/GJ; the prices of low-pressure steam (LPS) and medium-pressure steam (MPS) are denoted as  $C_{\text{Steam}}$  while  $C_{\text{Steam}}$  is 7.78 US\$/GJ for LPS and 8.22 US\$/GJ for MPS.

In this work, the single-stage steam jet ejector is used in the vacuum system and its cost can be calculated according to the following equations [5],

$$C_{vs} (\text{US\$}) = 1640 \times \left( \frac{M}{P} \right)^{0.41} \quad (S7)$$

$$M (\text{lb/hr}) = 5 + \left\{ 0.028 + 0.03088 [\ln(P)] - 0.0005733 [\ln(P)]^2 \right\} \cdot \left( \frac{V_C}{0.0283168} \right)^{0.66} \quad (S8)$$

$$V_c (m^3) = \frac{\pi}{4} \cdot ID^2 \cdot H \quad (S9)$$

$$C_{s,100\text{pisg}} (US\$) = \frac{10 \times M}{1000} \times 5 \times 8000 \quad (S10)$$

where  $C_{vs}$ ,  $M$  and  $P$  are the capital cost of the vacuum system (US\$), the air leakage rate (lb/hr) and pressure (torr), respectively.  $V_c$  and  $C_{s,100\text{pisg}}$  represent the volume of the column and cost of the steam with a pressure of 100 pisg, respectively.

## References

1. Yang J, Pan X, Yu M, Cui P, Ma Y, Wang Y, Gao J. Vapor–liquid equilibrium for binary and ternary systems of tetrahydrofuran, ethyl acetate and N-methyl pyrrolidone at pressure 101.3 kPa. *Journal of Molecular Liquids*, 2018, 268: 19-25
2. Yang A, Su Y, Chien I L, Jin S, Yan C, Wei S, Shen W. Investigation of an energy-saving double-thermally coupled extractive distillation for separating ternary system benzene/toluene/cyclohexane. *Energy*, 2019, 186: 115756
3. Luyben W L. *Distillation design and control using Aspen simulation*. 1st ed. New Jersey: John Wiley & Sons, 2013, 87-89
4. Yang A, Sun S, Shi T, Xu D, Ren J, Shen W. Energy-efficient extractive pressure-swing distillation for separating binary minimum azeotropic mixture dimethyl carbonate and ethanol. *Separation and Purification Technology*, 2019, 229: 115817
5. Seider W, Lewin D, Seader J, Widagdo S, Gani R, Ming N, *Product and process design principles: Synthesis, analysis and evaluation*. 4th Edition. United States: John Wiley & Sons: 2017